CAM-7/LTO Cells for Lithium-Ion Batteries with Rapid Charging Capability at Low Temperature

David Ofer, Leah Nation, Sharon Dalton-Castor, Brian Barnett, and Suresh Sriramulu
TIAX LLC
35 Hartwell Avenue
Lexington, MA 02421

Abstract: *TIAX is developing laminated prismatic lithium-ion (Li-ion) cells capable of rapid charging at low temperature (to -50 °C) to replace current lead-acid vehicle batteries. The novel cells are based on TIAX's high energy, high power CAM-7 cathode material, high rate capability lithium titanate (LTO) anode material, and a nitrile-cosolvent electrolyte formulation, and target cell-level energy content greater than 90 Wh/kg and 250 Wh/l.*

Keywords: laminate packaging; lithium-ion; low-temperature electrolyte, CAM-7; lithium titanate.

Introduction

Military applications can require rechargeable batteries to operate in extreme environments with temperatures as low as -50 °C or as high as 70 °C. These temperature extremes extend beyond those to which current commercial Li-ion technology is constrained, and are a major hindrance to replacement of current lead-acid vehicle battery technologies with much lighter, more compact Li-ion batteries. Prismatic laminate type lithium-ion rechargeable cells are of particular interest to the military because of their potential for dual-use application in both military and commercial automotive vehicles.

Operational temperature limitations of Li-ion batteries are related to the electrolytes and materials they use. At low temperatures, performance is hampered by low electrolyte conductivity and poor electrochemical kinetics associated with ion-desolvation processes.[1] Low-temperature charge acceptance capability is particularly poor because the graphitic carbon anodes used in Li-ion cells are particularly prone to plating lithium metal when charged at low temperature: a condition giving rise to rapid fade and serious safety concerns. At high temperatures, Li-ion battery lifetime is compromised by thermal instability of the electrolytes and of electrode surface films they form, and by the electrolytes' reactivity with the charged electrode materials; in particular by decomposition reactions at the graphitic carbon anode.[2] Furthermore, the high-temperature electrolyte decomposition reactions of Li-ion electrolytes form gaseous products. This gassing limits the use of laminated prismatic pouch cell designs, which are otherwise very advantageous for their light weight and easy form factor reconfiguration.

Accordingly, in a TARDEC-sponsored program, TIAX is developing low-temperature-capable, laminated prismatic lithium-ion cells employing TIAX's high energy, high power CAM-7 cathode material, high rate capability lithium titanate (LTO) anode material, and a nitrile-cosolvent electrolyte formulation. CAM-7 provides the highest energy content and rate capability of any market-ready cathode material. Commercially available nanostructured LTO is used for its high rate capability and its high potential vs. Li, enabling it to be lithiated at high rate and low temperature without plating lithium metal. Nitrile-cosolvent electrolyte provides outstanding performance at low temperatures and suppresses electrolyte gassing in foil laminate-packaged cell designs.

Cell Chemistry

CAM-7: TIAX's CAM-7 is a stabilized $LiNiO_2$-based cathode material offering an outstanding combination of high capacity and high rate capability as shown in Figure 1.

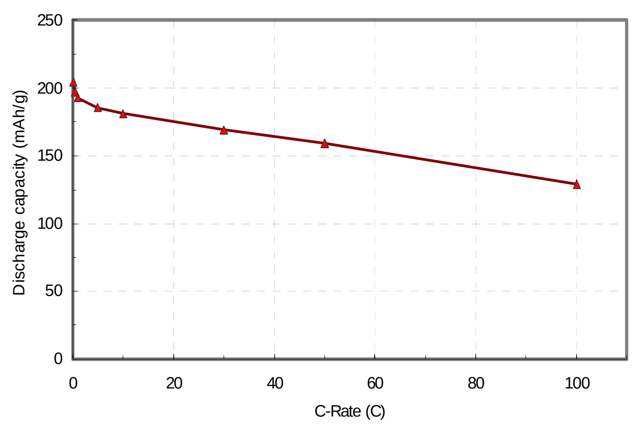

Figure 1. Discharge rate capability of CAM-7 in low loading (~2 mg/cm^2) Li metal half cells with all-carbonate electrolyte on basis of 200 mAh/g 1C rate.

CAM-7 has low levels of gas generation, facilitating its use in prismatic and laminate-packaging cell formats. CAM-7 evolves less gas than either commercial NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) or LCO ($LiCoO_2$) as shown by Figure 2, which compares results for gas evolution tests of charged cathode in contact with electrolyte.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
06 APR 2012	**Journal Article**	**01-03-2016 to 05-04-2012**

4. TITLE AND SUBTITLE
CAM-7/LTO Cells for Lithium-Ion Batteries with Rapid Charging Capability at Low Temperature

5a. CONTRACT NUMBER
w56hzv-11-c-0034

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
David Ofer; Leah Nation; Sharon Dalton-Castor; Brain Barnett; Suresh Sriramulu

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
TIAX LLC,35 Hartwell Ave,Lexington,MA,02421

8. PERFORMING ORGANIZATION REPORT NUMBER
; #22795

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army TARDEC, 6501 East Eleven Mile Rd, Warren, Mi, 48397-5000

10. SPONSOR/MONITOR’S ACRONYM(S)
TARDEC

11. SPONSOR/MONITOR’S REPORT NUMBER(S)
#22795

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Work performed under a Phase I ARMY SBIR.

14. ABSTRACT
TIAX is developing laminated prismatic lithium-ion (Li-ion) cells capable of rapid charging at low temperature (to -50 ?C) to replace current lead-acid vehicle batteries. The novel cells are based on TIAX?s high energy, high power CAM-7 cathode material, high rate capability lithium titanate (LTO) anode material, and a nitrile-cosolvent electrolyte formulation, and target cell-level energy content greater than 90 Wh/kg and 250 Wh/l.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Public Release**	**4**	

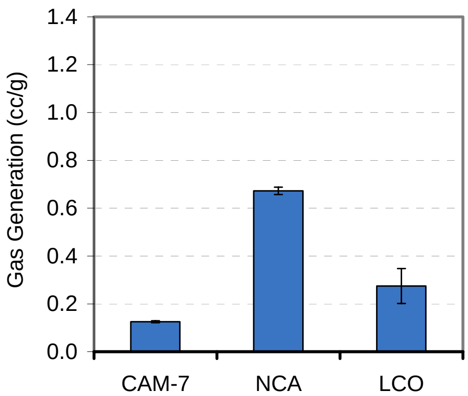

Figure 2. Comparison of gas generated from charged active materials in contact with all-carbonate-solvent electrolyte.

TIAX has installed a 50 metric ton per year CAM-7 pilot plant in Massachusetts. CAM-7 is being sampled to many of the prominent domestic and foreign battery manufacturers and developers for both vehicle and consumer electronics applications.

LTO: Although graphitic carbon is the predominant Li-ion anode active material, it can not be lithiated (as in Li-ion cell charging) at high rates or low temperatures without a high probability of undesirable Li metal plating because its potential is close to that of Li. $Li_4Ti_5O_{12}$ or LTO anode material was initially noted for its negligible volume change during electrochemical cycling, earning it designation as a "zero strain material,"[3] and giving it exceptional cycling stability. Nano-structured LTO is capable of exceptionally high rate capability and can be lithiated (charged) very rapidly, at least in part because at its high potential (~1.55 V vs. Li), passivating film (SEI) does not form on its surface. Therefore high surface area (nano) LTO can be used without incurring high 1st cycle irreversible capacity loss, and the lack of an SEI and its associated impedance enhances LTO rate capability. LTO's high potential enables it to be charged at high rates without danger of Li plating, as illustrated by Figure 3.

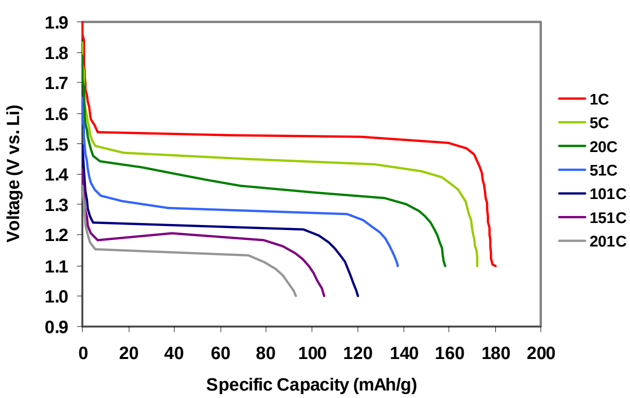

Figure 3. Ambient temperature half cell lithiation profiles as function of C-rate (1C = 170 mA/g) for LTO electrodes with 0.07 mAh/cm^2 active material loading. Commercially available LTO was fabricated into electrodes at TIAX.

Although LTO has very attractive attributes with respect to stability and charging rate capability, its low capacity and high potential impose significant sacrifice of Li-ion cell energy. However, LTO remains the only truly commercially available Li-ion anode alternative to carbon materials and is the only material capable of being charged at very low temperatures, and thus the use of a cathode material with the highest possible energy content (CAM-7) together with suitable high rate capability helps offset the loss of cell-level energy content that comes with use of LTO.

Nitrile-cosolvent electrolyte: Current commercial Li-ion electrolyte compositions consist almost exclusively of $LiPF_6$ salt in mixtures of cyclic ethylene carbonate (EC) with various linear carbonates, having emerged as providing the best overall balance of properties for Li-ion batteries in consumer electronics.[4] However cells with these electrolytes generally do not have acceptable life at temperatures above 60 °C or acceptable performance below -20 °C because the thermal instability of $LiPF_6$ is deleterious at high temperatures, while the high freezing point and viscosity of EC, as well as its high activation energy for lithium ion desolvation, is deleterious at low temperature.

Nitrile solvents have many properties that make them attractive for use in electrolytes, in particular high dielectric constant, low viscosity, low freezing point and wide liquidus temperature range. Figure 4 below shows that butyronitrile (BN) cosolvent added to carbonate electrolytes significantly enhances their conductivity.

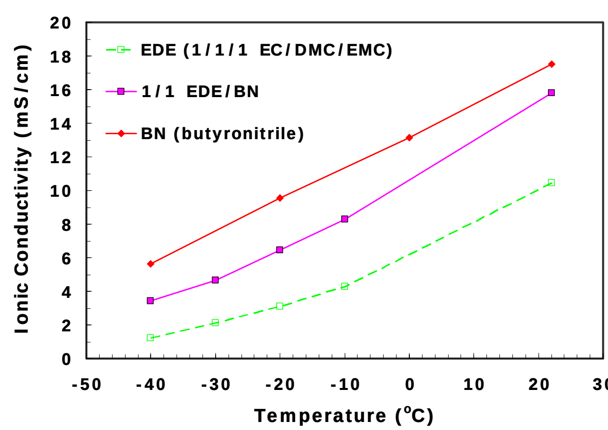

Figure 4. Ionic conductivity of 1 M $LiPF_6$ electrolytes composed of 1/1/1 EC/DMC/EMC formulated with BN cosolvent.

A further benefit of nitrile cosolvents is that they reduce the tendency of electrolytes to evolve gaseous decomposition products at elevated temperatures, a very advantageous feature for use in laminated packaging Li-ion cells.[5] Figure 5 below shows pressure vs. temperature results of measurements in an accelerating rate calorimeter for electrolytes heated to 85 °C at 5 °C/min, and held at that temperature for 48 hours before cooling back to ambient.

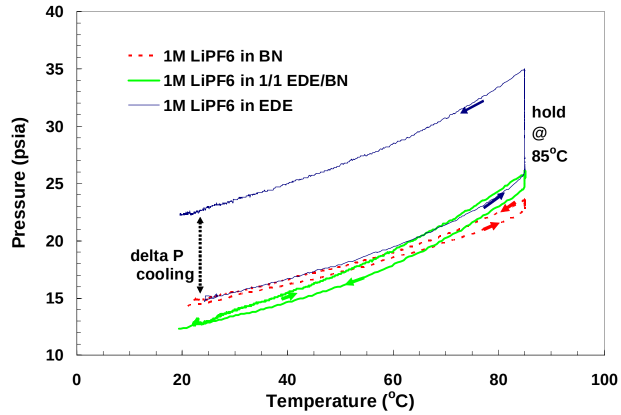

Figure 5. 85 °C non-condensable gas generation (from electrolyte decomposition) of 1M $LiPF_6$ electrolytes with conventional EDE, pure BN, or 1/1 EDE/BN solvents.

These tests are run in sealed vessels; any pressure increase measured upon cooling back to ambient temperature after 85 °C exposure is due to generation of non-condensable gases, and thus the figure shows that pure BN and BN-cosolvent electrolytes suppress non-condensable gas generation at high temperature, an attribute of potentially vital importance for laminate-packaged cells, which have very limited pressure containment capability. This benefit of nitrile cosolvents may be attributable to coordination of $LiPF_6$-derived PF_5 as has been demonstrated for nitrogenous Lewis bases,[6] which suppresses the tendency of PF_5 to oxidize the carbonate electrolyte solvents.

Cell Performance

Coin cells: Coin cell experiments demonstrate that excellent low-temperature performance is achieved by the CAM-7/LTO/nitrile-cosolvent electrolyte system. Figure 6 shows rate dependence of charge and discharge curves for a low loading CAM-7/LTO coin cell with 6/4 EDE/BN, 1M $LiPF_6$ electrolyte (EDEB64) at -47 °C.

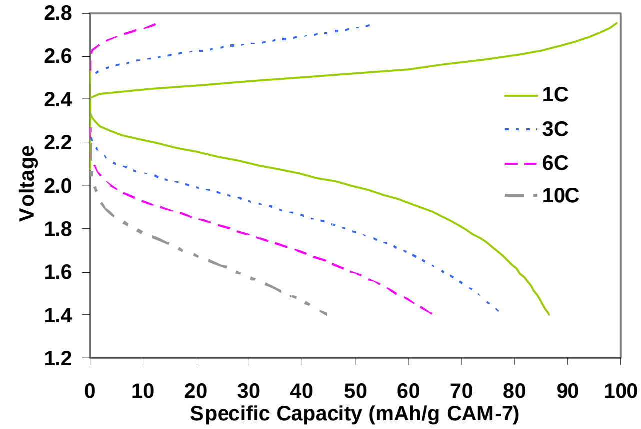

Figure 6. Rate dependence of -47 °C constant current charge and discharge (1C = 200 mA/g CAM-7) for 0.4 mAh/cm^2 CAM-7/LTO cells built with 1M $LiPF_6$ in 6/4 EDE/BN electrolyte.

Even using a standard (normal for ambient-temperature use) charge termination voltage of 2.75 V (corresponding to cathode potential of 4.3 V vs. Li), ~50% of full charge capacity (that full charge capacity being ~200 mAh/g CAM-7) is obtained in 1 hour, and almost 30% of charge capacity is obtained in 20 minutes at -47 °C, while much more capacity can be obtained if the voltage limit is raised. Almost 20% of the cell's intrinsic energy content can be delivered in 6 minutes for discharge to 1.4 V at -47 °C. Figure 7 compares capacities obtained with the 40% BN electrolyte to those obtained with proprietary compositions containing BN.

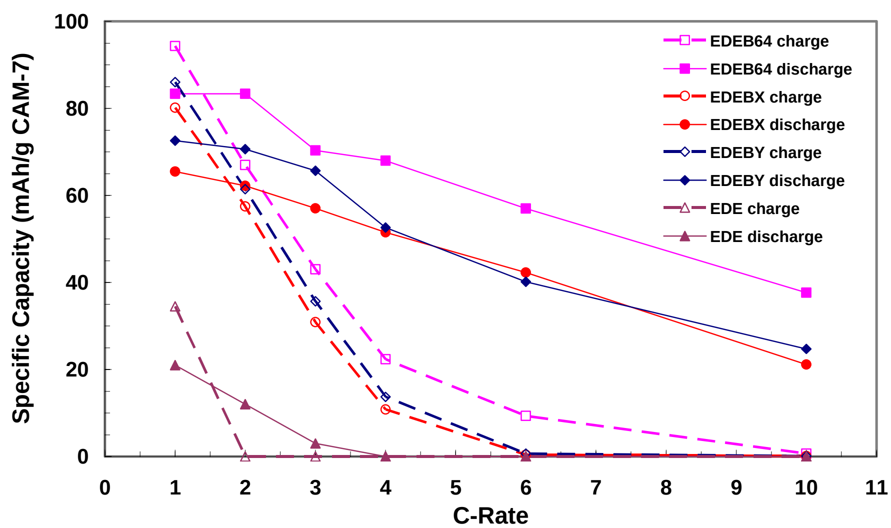

Figure 7. -47 °C rate capability (1C = 200 mA/g CAM-7) of CAM-7/LTO cells built with EDE electrolytes having varying BN cosolvent content and cycled between 2.75 V and 1.4 V.

Use of nitrile cosolvent reduces high temperature cycle life, however the relative benefit to low-temperature performance outweighs the impact on elevated temperature life, as can be seen by comparing the difference between data in Figure 7 for performance of EDE and EDEBY cells at -47 °C to the difference between data for capacity retention at 70 °C of cells made with both electrolytes, Figure 8. We are optimizing the electrolyte composition further to enhance the high temperature cycle life.

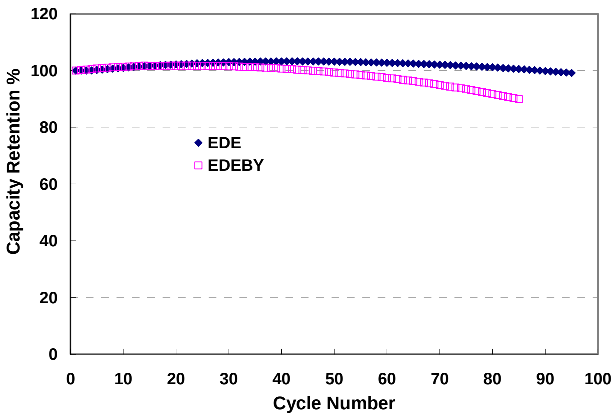

Figure 8. Capacity retention for 70 °C 2C/2C (1C=200 mA/g CAM-7) cycling of CAM-7/LTO (1.1 mAh/cm^2 electrode loading) Li-ion cells with EDE and EDEBY electrolytes.

Laminate-packaged cells: Preliminary laminate-packaged prismatic cells have demonstrated that the CAM-7/LTO/nitrile-cosolvent electrolyte system is compatible with implementation in laminated packaging and form factors. Figure 9 shows C/20 discharge curves for a CAM-7/LTO laminate cell at low temperatures.

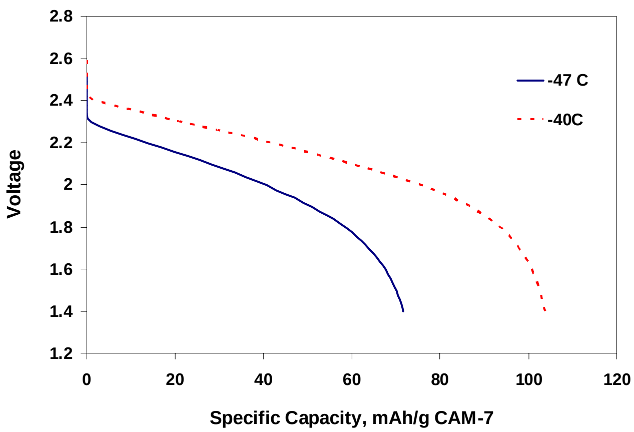

Figure 9. C/20 discharges at -40 °C and -47 °C for a 0.75 mAh/cm^2 CAM-7/LTO laminate cell made with EDEBY electrolyte.

TIAX is currently developing cell design and assembly techniques that will yield laminate cells with performance comparable to that already demonstrated in coin cells. Design models show that such laminate cells can achieve energy content in excess of 90 Wh/kg and 250 Wh/l.

Conclusions

Laminated Li-ion cells capable of being charged at temperatures approaching -50 °C based on CAM-7 cathodes, LTO anodes and electrolyte formulated with nitrile cosolvent are feasible. Optimal nitrile-cosolvent-based electrolyte formulations must balance improvements obtained in low-temperature performance and charging capability against dminution of high-temperature cycle life, however results to date suggest that dramatic improvements in extreme low-temperature performance can be achieved at relatively modest cost to elevated-temperature life.

Acknowledgements

TIAX thanks the US Army TARDEC for funding under Phase I SBIR contract # W56HZV-11-C-0034.

References

1. Kang Xu, “Charge-Transfer” Process at Graphite/Electrolyte Interface and the Solvation Sheath Structure of Li^+ in Nonaqueous Electrolytes,” *Journal of the Electrochemical Society*, Vol. 154, no. 3, pp. A162-A167, 2007.
2. Michel Broussely in “Advances in Lithium-Ion Batteries,” W. van Schalwijk and B. Scrosati, eds., , Chapter 13, Kluwer Academic/Plenum, 2002.
3. Tsutamu Ohzuku, Atsushi Ueda, and Norihiro Yamamota, “Zero-Strain Insertion Material of $Li[Li_{1/3}Ti_{5/3}]O_4$ for Rechargeable Lithium Cells,” *Journal of the Electrochemical Society*, Vol. 142, no. 5, pp. 1431-1435, 1995.
4. Kang Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” *Chemical Reviews*, Vol. 104, pp. 4303-4417, 2004.
5. U.S. Patent 7,718,322B2 to Y.-B. Lee, E.-H. Song, K.-S. Kim, T.-S. Earmme, Y.-M. Kim, 2010.
6. Wentao Li, Christopher Campion, Brett L. Lucht, Boris Ravdel, Joseph DiCarlo, and K. M. Abraham, “Additives for Stabilizing $LiPF_6$-Based Electrolytes AgainstThermal Decomposition,” *Journal of the Electrochemical Society*, Vol. 152, no. 7, pp. A1361-A1365, 2005.